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COLOR STABILIZATION IN BULK-TINTED GLASS

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A method has been developed for stabilizing the optical characteristics of sheet float glass by introducing specially selected colorants into the batch, whose quantity is determined from the difference between the light transmission of two samples. The difference in the transmission of the samples ("the delta") is determined for each wavelength, and a plot is constructed for the wavelength. Based on the peaks in the delta curve it is possible to identify differences in the transmission of glass samples of different thickness.

Producers of bulk-tinted glass with preset optical characteristics (color and light transmission) inevitably confront the problem of implementing a transition from one color to another and vice versa. Furthermore, it is essential to be able to produce at different times glasses of different thickness and yet an identical tint. The Technical Standards developed at the Saratov Institute of Glass standardize the light engineering parameters for glasses having different tints; for each color five or more color shades are specified, which have to strictly complied with when producing products at different times.

The problem becomes even more acute when substandard materials are used, as the available resources of natural minerals satisfying the stringent requirements of high-quality glass production are limited. When one material grade is replaced by another or when the content of iron oxide is unstable, the temperature of the inner glass melt layers may increase and shift the gas equilibrium in the melt, which produces bubbles in finished glass. An increased translucence of the glass melt may modify the temperature gradient, which impairs the melt homogeneity. The more perceptible the glass inhomogeneity (laminar inhomogeneity), the worse are the optical parameters.

An inhomogeneous distribution of glass density in time or across the glass ribbon as well may be a consequence of a substandard material or a batch with deviations above the permissible limits. As the iron oxide content grows, the glass melt density increases and the velocity gradient of surface currents grows as well. Therefore, fluctuations of iron content in glass are regarded as one of the possible reasons for an unstable quality of the finished product caused by changing heat transfer in the glass melt. A method is known for correcting the batch composition by introducing iron oxide compounds to stabilize the content of iron oxide in glass [1].

The instruction for the calculation of the amount of iron-bearing batch additives is based on determining their maximum content for stabilizing the preset content of Fe_2O_3. This instruction uses data on analysis of materials and glass for 1 – 2 years. However, this method is unacceptable when using substandard materials with frequent significant and unpredictable fluctuations of the chemical composition and is insufficient for the production of tinted glass.

In order to stabilize glass quality and obtain prescribed constant optical parameters, traditional colorants are introduced into the batch: nickel and cobalt oxides, metallic powders (iron, selenium, etc.) responsible for tinting and light transmission of glass.

Tint and light- and heat-shielding properties of glass depend on a certain ratio between the metallic colorants (selenium, oxides of cobalt, iron, and titanium) in glass. Practical studies carried out at the Saratov Institute of Glass indicate that within the entire light transmission range of glass (49 – 53%) the quantity of added selenium and cobalt has no significant effect on the light transmission of bronze glass in the IR spectrum. The content of FeO in glass has the maximum effect: the higher this content, the lower the transmission in the IR range.

The transmission in the visible spectrum range significantly depends not on the absolute content of FeO, $Fe_2O_{3\,tot}$, Se, and Co, but on the ratio between these elements [2]. The specified colorants used in glass melting have a certain absorption range and their effect is well observed on the spectral transmission curves of glasses (Fig. 1) [3].

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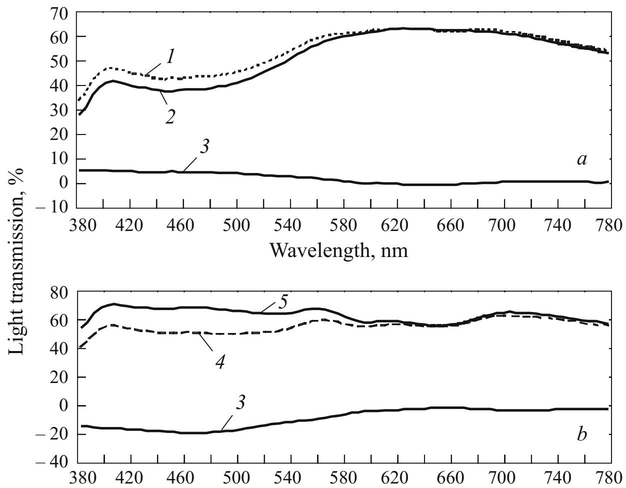

Fig. 1. Light transmission in the visible range of glasses in transition to the production of a dark-colored glass (*a*) and to another tint (*b*): *1*) bronze glass; *2*) glass TB-3; *3*) "delta" curve; *4* and *5*) gray and light blue glasses, respectively.

The main purpose of an industrial laboratory in the continuous production of tinted glass is to stabilize its optical parameters. The industrial laboratory at the Saratov Institute of Glass implements daily monitoring of light transmission in the visible (380 – 780 nm) and IR (760 – 1300 nm) spectrum ranges for the purpose of tint correction. Glass samples rarely are of equal thickness; consequently, to compare their integral light transmission, the method of conversion to a required thickness is used, which yields light transmission values with a certain error and is unacceptable comparing color shades.

In order to obtain the prescribed optical characteristics of glass in continuous production, the integral light transmission in the visible and IR spectra is determined by the wavelengths using a spectrophotometer on samples consecutively taken in time, and light transmission curves are plotted with an interval of 10 nm. The concentration of iron (II) oxide is calculated based on the transmission in the IR range, i.e., the integral transmission in a narrow spectrum segment in the range of the absorption band of iron (II) oxide. The total content of iron oxides (Fe_2O_3) is found by the chemical method. The numerical values of the transmission of the samples in the visible spectrum range with an interval of 10 nm are listed in a table; the transmission difference is determined for each wavelength, then the plot of the variation in the light transmission difference of two samples depending on the wavelength is constructed. Based on the curve peaks we reveal the transmission differences between the two glass samples for each wavelength. In the perfect case of the coincidence of spectral characteristics this curve is a straight line.

Figure 1*a* shows the transmission curves of bronze glass and a darker glass TB-3, as well as the transmission difference curve for the two glasses: the "delta curve." The delta curve in the wavelength range above 580 nm and the IR range approaches a straight line and corresponds to "zero"; consequently, the glass tint needs to be corrected in the visible range up to 580 nm. We see a similar delta curves in Fig. 1*b*, where the light transmission of two glasses is equal within the wavelength range of 620 – 780 nm. Yet such coincidence is registered in a perfect case with the equal thickness of the samples considered. In the case of glasses with an identical tint but different thickness, the delta curve should be a straight line intersecting the ordinate axis at a point depending on the difference in the sample thickness.

The obtained data are used to correct the batch formula taking into account the content of iron in the raw materials and glass cullet. The weight and the ratio of colorant additives is determined based on practical experience, production specifics, and the composition of glass [3], but to maintain the heat balance in the glass melt, the light transmission variation in the visible range should not exceed 1.5 – 2.0% per day during the correction process.

Thus, comparing the transmission of glass samples in the preset wavelength range, one can correct the color by adding a specially selected colorant, which decreases transmission in the particular spectrum range, thus bringing the transmission curves and the tint to total agreement.

Summarizing the above, let us list the main stages for converting a production line to producing glass of a different color:

– before the transition, spectral transmission curves in the visible range are registered for the reference glass and the glass currently produced on the line;

– the content of iron oxide in glass, batch, and recyclable cullet is determined;

– the quantity of the colorants required to obtain the specified color and light transmission is theoretically calculated;

– the changes in the glass and batch compositions are determined by stages; the glass light transmission variation is calculated theoretically and a product range for the transition period is planned;

– after the required amendments are introduced in the batch preparation process and, if needed, in the melting and working processes as well, one should monitor daily the variations in the optical parameters of the transitional glass and construct the delta curves, in order to achieve complete compliance of real parameters with the reference standard.

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